

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/hydro

Developing lithium ion battery silicon/cobalt core-shell electrodes for enhanced electrochemical properties

Tugrul Cetinkaya^{*}, Mehmet Uysal, Mehmet O. Guler, Hatem Akbulut

Sakarya University, Engineering Faculty, Department of Metallurgical & Materials Engineering, Esentepe Campus, 54187 Sakarya, Turkey

ARTICLE INFO

Article history:

Received 24 October 2013

Received in revised form

2 June 2014

Accepted 18 August 2014

Available online 10 September 2014

Keywords:

Si/Co nanocomposite

Core-shell

EIS

Cyclic voltammetry

Discharge capacity

ABSTRACT

In this work, core-shell Si/Co composite powders were produced using an electroless deposition process. The effect of different concentrations of CoSO_4 in the plating bath was studied to provide the Co deposition and to reveal the structure on the surface of silicon powders. The surface morphology and the composition of the produced Si/Co composite powders were characterized using scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) analysis was performed to investigate the structure of the Si/Co composite powders. The discharge capacities of Si/Co composite electrodes were determined with cyclically testing, and resistivity of the produced Si/Co composite electrodes were studied using electrochemical impedance spectroscopy (EIS). The silicon/cobalt composite electrode produced using 40 g/L CoSO_4 exhibited the most stable capacity retention, and a discharge capacity of approximately 220 mAh/g was obtained after 15 cycles for this electrode. This study demonstrated that the conductivity of the electrodes was improved and the capacity retention of the Si/Co composite electrodes was increased by increasing the shell structured cobalt content on the surface of silicon powders due to the buffering effect of cobalt against huge volume changes during the lithiation and delithiation process.

Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

Introduction

The energy always played an important role in human being's life [1]. In today's world, there is a high demand for electrical energy storage devices for stationary and mobile applications such as uninterrupted power supply, voltage regulations, electric vehicles (EVs) and hybrid electric vehicles (HEVs) [2]. Lithium-ion batteries (LIBs) have attracted considerable research interest since their introduction in the early 1990s.

This is mainly due to the higher energy density compared to other competing battery systems such as nickel-metal hydrides and nickel cadmium batteries. Lithium batteries are acclaimed as advanced power sources that could provide power for mobile phones, computers, electric vehicles, satellites, militaries etc., and it has already captured a large share of the market [3,4]. Recently, a large amount of interest has been attracted to the anode materials for lithium ion secondary batteries, which can replace conventional graphite anode to improve battery performance. Promising candidate

^{*} Corresponding author. Tel.: +90 555 6233694; fax: +90 264 2955601.

E-mail addresses: tetinkaya@sakarya.edu.tr, tugrulcetinkaya@gmail.com (T. Cetinkaya).

<http://dx.doi.org/10.1016/j.ijhydene.2014.08.080>

0360-3199/Copyright © 2014, Hydrogen Energy Publications, LLC. Published by Elsevier Ltd. All rights reserved.

materials for anode are considered as Sn, Si, and LTO ($\text{Li}_4\text{Ti}_5\text{O}_{12}$), and carbons with diverse structures [5,6]. Among those anode materials, silicon is one of the most attractive anode materials because it has a large theoretical specific capacity of 4200 mA h g^{-1} [7]. However, large volume changes occur in Si during Li-insertion and extraction, which causes pulverization of the active materials followed by a loss of electrical contact. As a result, the Si electrodes show a rapid capacity fade [8]. To overcome this problem, researchers have focused on improving the conductivity and ductility of silicon anodes with coating surface of silicon powders by an inactive matrix such as Cu, Ni and Co. It has been reported that coating the surfaces of silicon with a high conductivity material such as copper and nickel can remarkably improve both the conductivity and cycleability of the silicon electrode. Recently, several studies are being reported as anode materials for LIBs considering Si/Cu and Si/Ni composites. It was reported that coating of the surface of silicon powders with Ni or Cu provided to support the electrode against mechanical disintegration, to increase the cycling efficiency and the rate capability, to minimize overall capacity loss, to improve the conductivity and promotes charge transfer of the silicon electrode [9–12].

As mentioned above, there are many studies for improving electrochemical performance of the silicon electrode by using inactive materials. Recent studies also indicate that Co coating can be applied on silicon surface to improve electrochemical properties of the silicon. It was prepared nanomountains (NMAs) array supported silicon film anode [13] and concluded Co NMAs facilitate the charge collection and transport, support the electrode structure as inactive confining buffer. This study showed that cobalt coating on the surface of silicon particles, also is an effective way to enhance electrochemical properties of the silicon. However, these studies generally employed physical vapour sputtering techniques or complex chemical synthesis techniques to coat the surfaces of the silicon electrodes.

We herein report on a simple, cost-effective, and acceptable approach for synthesizing cobalt-coated silicon particles using an electroless coating method to obviate electrode pulverization, emanated from large volume increase during lithiation. Although, there are many published papers in the literature about electroless cobalt coating, used for oxygen evaluation, for fuel cells [14,15], this study is the first for applying electroless cobalt coating on the surface of silicon powders for LIBs. In this study, the Co-coated silicon particles in a core-shell structure were utilized as the active anode material in LIBs half-cells and effect of deposited cobalt content was investigated on the electrochemical performance of Si/Co composites. Our results demonstrate that coating silicon with cobalt facilities highly reversible and increased charge storage capacity, and improved tolerance to volumetric expansion/contraction processes upon cycling.

Experimental methods

In this study, the silicon powders supplied from Alfa Aesar (purity 99.5%, between 1 and $20 \mu\text{m}$ in size) used to produce Si/Co composite powders. Before producing the Si/Co composite

powders using an electroless process, the surface of the silicon powders were pretreated to achieve catalytic activity. First, the surfaces of the silicon powders were cleaned with acetone to remove the contaminants. The surfaces of the silicon powders were then sensitized with 15 g/L SnCl_2 and a 60 mL/L HCl (hydrochloric acid, concentration of 37%) solution under magnetic stirring for 30 min. The silicon powders were then activated in a solution containing 0.75 g/L PdCl_2 and 15 mL/L HCl under slow stirring with a magnetic stirrer for 30 min. Finally, the silicon powders were filtered and washed with distilled water several times. The pretreatment of the silicon powders was completed after drying the activated powders for 10 h in a vacuum oven at 60°C .

After the pretreatment process, the surfaces of the silicon powders were coated with cobalt (Co) using an electroless process. An electroless bath was prepared using a CoSO_4 precursor; the composition of the electroless bath and the plating conditions are presented in Table 1. In this bath, the concentration of CoSO_4 was varied to investigate the effect of the CoSO_4 concentration on the coating morphology, coating uniformity and the deposited cobalt content on the surface of the silicon powders. The plating process was performed at 50°C , and the plating time was maintained constant at 5 min for all the samples. The pH value of the plating bath was controlled continuously during plating to fall between 8 and 9 using NaOH as a buffer agent. After the plating process, the cobalt-coated silicon particles were rinsed with distilled water and then dried at 60°C in a vacuum oven for 12 h. The weight difference of the silicon powders before and after plating was measured using an analytical balance with $\pm 0.1 \mu\text{g}$ precision. The weight gain of the Si/Co composite powders was expressed using the formula $\Delta W = W_i - W_o$, where W_i and W_o are the weight of the Co-coated silicon powders and uncoated silicon powders, respectively. The experiments for coating the surface of the silicon powders and determining the weight difference of the cobalt-coated silicon powders after the plating process were repeated several times to optimize the experimental parameters and provide reproducibility for the coatings.

The surface morphology of the cobalt-coated silicon powders was characterized using SEM (JEOL 6060 LV) equipped with EDS. Possible growth planes and the crystallographic relationship of the Si/Co composite powders were determined from XRD patterns using a Rigaku D/MAX 2000 X-ray diffractometer with Cu $K\alpha$ radiation. The diffraction patterns were recorded in the step-scan mode and recorded at 1° (2θ) steps

Table 1 – Chemical compositions of the electroless cobalt plating bath.

$\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	10 g/L, 20 g/L, 40 g/L
Na-citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$)	90 g/L
H_3BO_3	45 g/L
$\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$	8 g/L
Powder concentration	10 g/L
Time	5 min
pH	8–9
Temperature	50°C
Stirring speed	200 rpm

Download English Version:

<https://daneshyari.com/en/article/7717053>

Download Persian Version:

<https://daneshyari.com/article/7717053>

[Daneshyari.com](https://daneshyari.com)